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厚膜用導電ペースト

(54)[TITLE]

The electroconductive paste for thick films

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【明細書】

[SPECIFICATION]

【1.発明の名称】

[1. TITLE]

厚膜用導電ペースト

The electroconductive paste for thick films

【2.特許請求の範囲】

Ag,Pd,Au,Pt 等の貴金属粉末が49~91 重量%と,ガラスフリットが6~20 重量%と,Zn,Al,Sn の1 種以上からなる粉末が3~31 重量%とからなるものをバイダーで粘結させてなることを特徴とする厚膜用導電ペースト。

【3.発明の詳細な説明】

【産業上の利用分野】

この発明は、いわゆるスクリーン印刷法等の厚膜法により、混成集積回路等を製造するのに使用される導電ペーストに関する。

【従来の技術】

一般に厚膜法により混成集積回路等の回路装置を製造する場合は、貫通孔を有するセラミック 重通孔を有するとファクースの配法により、所電ペースとの が関係して、の配えり、所電ペースを が関係して、の配えり、所電ペースを が関係して、の配えり、の記されたが が見いると共に、同し、これが に充すしたが採用さたが にたさたが にたさたが にたさたが にいる。

導電ペーストを空気中で焼成する場合,金属成分の酸化にたる属成分を防止を防止を防止を防止を防止を防止を関係を関係を関係を関係した。 お抗値の増化を原を対した。 が、Ag,Au,Pt等の場合が、これをはのは、 が、これのは、これのでは、 をののでは、これのでは、 をののでは、 のののでは、 のののでは、 ののでは、 のの

しかし,上記基板の上に被膜抵

[2. Claim]

That which consists of noble metal powders, such as Ag, Pd, Au, and Pt, of 49 - 91 weight%. glass frit of 6.- 20 weight%, and powder which consists of 1 or more sorts of Zn, Al, and Sn of 3 - 31 weight%, is made to cake with a binder.

The electroconductive paste for thick films characterized by making as above-mentioned.

[3. DETAILED DESCRIPTION OF INVENTION]

[INDUSTRIAL APPLICATION]

This invention relates to the electroconductive paste used for producing a hybrid integrated circuit etc. by thick film methods, such as the so-called screen printing method.

[PRIOR ART]

When circuit apparatuses, such as a hybrid integrated circuit, are generally produced by the thick film method, the method in which while according to a predetermined wiring pattern, an electroconductive paste is printed by the screen printing method, using the ceramic substrate which has a through-hole as a base, the above through-hole is filled with said paste, and these are printed is adopted.

When baking an electroconductive paste in air, in order to prevent the gain of the resistance value by the oxidation of a metal component, the electroconductive paste which essentially consists of noble metals, such as Ag, Au, and Pt, is used. However, these are expensive.

Then the method of using the electroconductive paste which essentially consists of base metal, such as Ni, and baking this in inert gases, such as N2 gas, as an object for inexpensive, is utilised.

However, baking in air the resistive paste which essentially consists of RuO2 used in order to compose a film resistor on an above substrate is needed.

For this reason, when a film resistance is

composed, after baking processing the electroconductive paste which essentially consists of base metal, the base metal conductor exposed externally was galvanized with noble metals for anti-oxidation. Then, the electroconductive paste and the above resistive paste which essentially consists of noble metals are printed from on this. The method of printing this in air was taken.

【発明が解決しようとする問題 点】

この発明は、上記の従来の問題を を解消すべるとガラストにとがラストにるとガラストにるとガラストにるので、 を解消する導電ペース加えるでは ないのので、 はいのので、 ないのので、 はいののので、 はいのので、 はいのので、 はいののでとに、 はいののでとに、 はいのののでとに、 はいのののでとに、 はいのののでとに、 はいのののでとに、 はいのののでとに、 はいのののでとに、 はいのののでとに、 はいのののでといる。 を属すででで、 はいののででで、 はいののででで、 はいののでで、 はいののので、 はいののので、 はいののでで、 はいのので、 はいのので、 はいののので、 はいのので、 はいのので、 はいのので、 はいのので、 はいのので、 はいのので、 はいのので、 はいののででで、 はいののででで、 はいののでで、 はいののでで、 はいののでで、 はいののでで、 はいののでで、 はいののでで、 はいののでで、 はいののでで、 はいののでで、 はいののででで、 はいののでで、 はいののでで、 はいののでで、 はいのので、 はいのので、 はいのので、 はいのでで、 はいのでで、 はいのので、 はい

[PROBLEM ADDRESSED]

However, in the anti-oxidation process by noble metals plating, the procedure which carries out plating of the it top with noble metals first after giving Ni plating only to the base metal conductor exposed to the surface of a ceramic substrate is taken.

Accordingly a relatively complicated process is needed. This is why the cost reduction effect obtained by using a base metal paste is eliminated sharply.

This invention is made that the above-mentioned conventional problem should be eliminated. It paid attention that there is an effect which prevents an oxidation by the boundary surface of said base metal conductor when applying a coating and baking processing this on the surface of a base metal conductor, by adding a small amount of Zn, Al or Sn to noble metals and the electroconductive paste which consists of the glass frit. A direct electroconductive paste is printed, without carrying out a special anti-oxidation process, such as noble metals plating etc. It enables it to bake this in air.

【問題を解決するための手段】 この発明による厚膜用導電ペーストは,Ag,Pd,Au,Pt等の貴金属 粉末が 49~91 重量%と,ガラスフリットが 6~20 重量% と,Zn,Al,Snの1種以上からなる 粉末が 3~31 重量%とからなる ものである。

ガラスフリットには,CaO-BaO-SiO2 系ガラス等の硼珪酸ガラスが一般に使用される。

【作用】

これは次ぎのような理由によ るものと考えられる。上記導電 ペーストが空気中で焼成される と,卑金属導体との界面付近に 存在する Zn,Al,Sn 等の金属が 同卑金属導体から酸素を奪って 酸化され,これが焼結されたガ ラス成分中に取り込まれるよう にして分散する。このため、卑金 属導体の表面付近では,その中 の Ni 等の金属成分がいわば還 元状態となり,これが酸化され ずに上記導電ペースト中の Ag,Pd,Au,Pt 等の貴金属成分と 反応して電気的導通状態を形成 する。

なお,導電ペーストの組成比を上記のように限定した理由は,

[Means for solving a problem]

The electroconductive paste for thick films by this invention, consists of noble metal powders, such as Ag, Pd, Au, and Pt, of 49 - 91 weight%, glass frit of 6 - 20 weight%, and the powder which consists of 1 or more sorts of Zn, Al, and Sn is 3 - 31 weight%.

Borosilicate glasses, such as CaO-BaO-SiO2-based glass, are generally used for the glass frit.

[EFFECT]

When the electroconductive paste by this invention is used, noble metals plating is not made to the surface of the base metal conductor baked in the inert gas, but said paste is directly printed in piles on this. This is baked in air.

Then, the conduction state required for electric connection of a circuit is obtained at the contact of a base metal conductor and the conductor which bakes an above electroconductive paste and was obtained).

This is considered to be caused the reason below.

If an above electroconductive paste is baked in air, metals, such as Zn, Al, Sn, etc. which exist near the boundary surface with a base metal conductor, will take oxygen from said base metal conductor, and will oxidize. In the glass component by which the sintering was carried out, this is received and makes and disperses.

metal conductor, metal components, such as Ni in it, will be, so to speak, in the reduction state. This is not oxidized, but reacts with the noble metals components in an above electroconductive paste, such as Ag, Pd, Au, and Pt, and an electric conduction state is formed.

In addition, the reason which limited the composition ratio of an electroconductive paste as mentioned above is as following.



次ぎの通りである。

(1)Zn,Al,Sn 等の金属粉末が多いと,導電ペーストををといるを変化物のを展光を変化物を見たときに生じる酸化物でののが多点に分したとったの。 が多くなるため、同時のでは物でのでのがる。 結果,導体の接着またがラストでのがるがでの。 結果,導体のをでは、ガラストでのがるができた。 は、カーンでは

(2)ガラス成分が少な過ぎると 導体間の接着強度が低くなり、 逆に多過ぎると焼結されたガラ ス成分が導体間の接合面を覆 い、導体間の接触抵抗が高くな る。この点から 6~20 重量%の 組成比が必要である。

【実施例】

次ぎにこの発明の実施例を説明する。Ag 粉末 63g,Pd 粉末 12g,Zn 粉末 6g 及び CaO-BaO-SiO2 系ガラスフリット 19g にバインダーとしてエチルセルローズ 6g と α -ターピネオール 33g を加え,3 段式ロールミルで混練し,別表の試料番号 55 で示された組成を有する導電ペーストを作った。

さらにこの他にも同様の方法で,別表の試料番号3~5,7~9,13~17,21,22,24~26,29~33,36~39,43~45,49,50,52,54~61,64~71,73~77,79~85で示された組成を有する導電ペースト

(1) If there are many metal powders, such as Zn, Al, and Sn, the quantity of the oxide produced when baking processing an electroconductive paste in air will increase. As a result of said oxide's dispersing so much in a glass component, there is trend that the adhesion strength of a conductor reduces.

Moreover, the above oxide which exists in a noble metals grain boundary, without dispersing in glass raises the resistance value of a conductor.

These need to be 31 weight% or less practically from this point.

Moreover the composition ratio requires 3weight% in the minimum in order to do an above effect so.

(2) If a glass component is too few, the adhesion strength between conductors will become low. Conversely if it is too much, the glass component by which the sintering was carried out will wear the connection surface between conductors, and the contact resistance between conductors will become high.

The 6 - 20-weight% composition ratio is required from this point.

[Example]

The Example of this invention is explained below.

Ethyl cellulose 6g and (alpha)- terpineol 33g is added as a binder to 63g of Ag powder, 12g of Pd powder, 6g of Zn powder and CaO-BaO-SiO2-based glass frit 19g. Kneading is carried out by the 3 step formula roll mill. The electroconductive paste which has the composition shown by the sample number 55 of the attached table was made.

Furthermore in addition to this, the electroconductive paste which has the composition shown by the sample number 3 - 5 of the attached table, 7 - 9, 13 - 17, 21 and 22, 24 - 26, 29 - 33, 36 - 39, 43 - 45, 49, 50 and 52, 54 - 61, 64 - 71, 73 - 77, and 79 - 85 was respectively made by the similar method.



をそれぞれ作った。

【使用例及び試験例】

次ぎに,上記実施例で得られた 導電ペーストを次ぎのような方 法で使用し,かつ試験を実施し た。

複数の貫通孔を有する厚さ 200 μ m の未焼結磁器シートに, 所定の配線パターンに従っ て、Ni を主成分とする導電ペー ストをスクリーン印刷すると共 に,貫通孔に上記導電ペースト を充填した。次いで,この未焼結 磁器シートを 125℃の温度で 10 分間加熱して乾燥した後,所定 の順序で 4 枚積層して圧着し た。次いでこれを 900℃の温度 で熱処理して磁器シート及び導 電ペースト中のバインダ成分を 除去した後.2%の H2 を含む N2 ガス雰囲気中で 1200℃の温度 下に 2 時間置き,図面に示すよ うな多層配線基板を作った。

この時点で基板 1.1・・・内部 で互いに導通する導体 2,2・・・ の抵抗値を,最上段の基板の表 面に露出した導体表面 2a,2b 間 において測定しておく。

次ぎに上記実施例で得られた 導電ペーストを使用し,最も外 側の基板 1 の表面に露出した導 体表面を覆うよう同ペーストを スクリーン印刷し、これを空気 中において 850℃の温度を 10 分間与えて焼成して導体 3.3 を 設けた。なお、この際、基板の端部 に 1mm 角の引き出し電極部 5 を設けた。

[Example of usage, and EXPERIMENT]

Next, the electroconductive paste obtained in the above Example was used by the method like the next, and the test was performed.

The through-hole was filled with the above electroconductive paste while the screen printing of the electroconductive paste which essentially consists of Ni is carried out on the non-sintered ceramic sheet of thickness 200 has some through-holes micro-m which according to a predetermined wiring pattern.

Subsequently, this non-sintered ceramic sheet is heated for 10 minutes at the temperature of 125 degrees C. After drying, 4 sheets were laminated in the predetermined order and it was stuck by pressure.

Subsequently this is heat-treated at the temperature of 900 degrees C. After removing a ceramic sheet and the binder component in an electroconductive paste, it puts for 2 hours at the temperature of 1200 degrees C in N2 gas atmosphere containing 2% of H2. The multilayer wiring board which is shown in the drawing was made.

At this time, the resistance value of a conductors 2 and 2*** which conduct mutually within substrate 1,1***, is measured between conductor surfaces 2a and 2b which were exposed to the surface of the substrate of the top stage.

Next the electroconductive paste obtained in the above Example is used. The screen printing of said paste is carried out so that the conductor surface exposed to the surface of the most outer substrate 1 may be covered. In air, the temperature of 850 degrees C is provided for 10 minutes, and this is baked. Conductors 3 and 3 were provided.

In: addition, the lead-out electrode part 5 of 1 mm square was provided to the terminal part of a substrate at this time.

次いで新たに設けられた導体 Subsequently the resistive paste which 3,3 間に互って RuO2 を主成分 essentially consists of RuO2 is printed between



とする抵抗ペーストを印刷し, これを空気中において 850℃の 温度を 10 分間与えて焼成し,基 板 1 の上に被膜抵抗 4 を作製し た。

そしてこの導体 3,3 と被膜抵抗 4 を作製する前後において、それぞれ上記導体 2,2・・・の抵抗値を,その上に新たに設けられた上記導体 3,3 の表面 3a,3bで測定した上記抵抗値を 2a,2b で測定した上記抵抗値との比は,何れも 1.00 であり,酸化雰囲気中で焼成しても抵抗値の増化はみられなかった。これを別表の導通性の欄に「〇」で示した。

また,上記電極部 5 に 0.5 φの リード線6を半田付け7し,同リ ード線6を基板1の表面に対し て垂直方向に引っ張って試験し たところ,別表に示す通り,同電 極部5が基板1表面から剥離す るときの引張強度は,何れも 1.0kg/mm2以上であった。

【比較例】

the conductors 3 and 3 provided newly. In air, the temperature of 850 degrees C is provided for 10 minutes, and this is baked. The film resistance 4 was produced on the substrate 1.

And before and after producing these conductors 3 and 3 and the film resistance 4, the resistance value of above conductors 2 and 2 *** is respectively measured on the surfaces 3a and 3b of the above conductors 3 and 3 which were able to be newly provided on it. The ratio with the above resistance value which measured this on the conductor surfaces 2a and 2b is 1.00. Even when it baked in the oxidizing atmosphere, the gain of resistance value was not seen.

"(circle-symbol)" showed this to the column of the conduction property of an attached table.

Moreover, the lead wire 6 of 0.5 (phi) is soldered to the above electrode part 5. When said lead wire 6 was pulled perpendicularly to the surface of a substrate 1, and tested, the tensile strength in exfoliating said electrode part 5 from the substrate 1 surface was 1.0kg /mm2 or more as shown in an attached table.

[Comparative Example]

For the sake of a comparison with an above Example, as shown in each column of the sample numbers 1, 2, 6 10 - 12, 18 - 20, 23, 27, 28, 34 and 35, 40 - 42, 46 - 48, and 51, 53, 62, 53, 72 and 78 of an attached table, the same component as the electroconductive paste by this invention is contained. However, the composition ratio makes the specimen which does not fulfill the requirements for above, like an above Example. This was used on the same conditions as the example of above usage and EXPERIMENT, and this was tested.

As this result, as shown in each column of an attached table, the ratio of the resistance value respectively measured between conductor surfaces 3a and 3b before and after production of conductors 3 and 3 and the film resistance 4.



導体表面 2a,2b 間で測定した抵抗値の比が 1.00 を越えるか(この抵抗値の比が 1.00 を越えるものを別表の導通性の欄に「×」で示した),または引張強度が1.0kg/mm2未満であった。

and the resistance value measured between conductor surfaces 2a and 2b exceeds 1.00 ("*" showed that by which the ratio of this resistance value exceeds 1.00 in the column of the conduction property of an attached table.) Or tensile strengths was 1.0kg / mm2 or less.

【発明の効果】

【4.図面の簡単な説明】

図面は、この発明による導電ペーストの使用例を示す多層配線 磁器基板の厚さ方向の寸法を拡大した概略縦断面図である。 特許出願人 太陽誘電株式会社 代理人 弁理士 北條和由 別表

* は比較例として作製された 試料を示す

試料番号 組成比(重量%) 導通性 引張強度 kg/mm2

硝子

[EFFECT OF THE INVENTION]

As having explained above, according to this invention, a direct electroconductive paste is printed so that the above conductor surface may be covered, without carrying out a special anti-oxidation process of giving noble metals plating to the surface of a base metal conductor. And only by baking this in air, the conduction property required to compose an electric circuit, without oxidizing the conductor surface can be obtained.

For this reason, the number of processes reduction for producing circuit apparatuses, such as a hybrid integrated circuit, can be aimed at now.

[4. Brief Description of Drawings]

A drawing is the schematic cross-sectional chart to which the dimension of the thickness direction of the multilayer interconnection ceramic substrate which shows the example of usage of the electroconductive paste by this invention was enlarged.

PATENTEE Taiyo Yuden Co., Ltd. K.K.
Representative Patent attorney Kazuyoshi
Hojo
Attached table

* shows the specimen produced as Comparative Example.

Attached table

Row (left to right): Sample number, Composition ratio (weight%) (glass), Conduction property, Tensile strength kg/mm2

* shows the specimen produced as Comparative Example.

DERWENT THOMSON SCIENTIFIC

*は比較例として作製された試 Row (left to right)

料を示す

試料番号

組成比(重量%)

導通性

Sample number. Composition ratio (weight%) (glass), Conduction property

引張強度 kg/mm2

硝子

*は比較例として作製された試

料を示す

試料番号

組成比(重量%)

kg/mm2 Tensile strength

shows the specimen produced Comparative Example.

Row (left to right) : Sample

Composition ratio (weight%) (glass),

導通性

引張強度 kg/mm2

硝子

*は比較例として作製された試

料を示す

試料番号

Conduction property, Tensile strength kg/mm2

specimen produced shows the as Comparative Example.

Row (left to right): Sample number,

組成比(重量%)

導通性

引張強度 kg/mm2

硝子

(図示しない)

Composition ratio (weight%) (glass), Tensile strength Conduction property. kg/mm2

(No drawing)

手続補正書

昭和 59 年 10 月 9 日

特許庁長官 志賀 学殿

1.事件の表示

昭和 59 年特許願第 187067 号

Amendment

October 9th, Showa 59

Director-General of the Patent Office Mr.

Manabu Shiga

1. Display of an incident

Patent application of No. Showa 59 187067

【2.発明の名称】

厚膜用導電ペースト

3.補正をする者

事件との関係 特許出願人

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2番12号

[2. TITLE]

The electroconductive paste for thick films

3. Person Who Corrects

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00/10/30

10/12

(C) DERWENT

町3丁目3番 氏名(8192)弁理士 北條和由 5.補正命令の日付 (自発)

5. Date of Correction Instruction (Spontaneity)

6.補正により増加する発明の数 7.補正の対象 明細書の発明の詳細な説明の欄 8.補正の内容 別紙の通り

Number of Invention Increased by Correction
 Objective of correction
 The column of the DETAILED DESCRIPTION
 OF INVENTION of Specification

8. Content of Correction
The attached sheet

補正の内容

(1) 明細書第 2 頁上から 4 行~ 上から 11 行の文章を次ぎの通 り補正します。

Content of a correction

(1) the sentences of 4th line of 2 page of specification from 11th line is corrected as follows.

"When baking electroconductive paste in air, in order to prevent the gain of the resistance value by the oxidation of a metal component, the electroconductive paste which essentially consists of noble metals, such as Ag, Au, and Pt, is used. However, these are expensive. Then the electroconductive paste which essentially consists of base metal, such as Ni, is used as an object for inexpensive. The method of baking this in inert gases, such as N2 gas, is utilised."

(2) "increasing" the 5th line from the bottom of the 8th page of Specification, is corrected to "an increase".

以上



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